Effect of Composition Variables on the UV Curing Behavior of Conductive Ink Formulations

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Abstract

Solvent-free UV-hardenable conductive ink formulations for printed microelectronics were designed to retain thermoplastic behavior after UV exposure. The binder system consists of a monofunctional liquid acrylate monomer along with an acrylic resin as viscosity modifier/ stabilizer for conductive particles. Conductive fillers used for this system were different types of silver particles in the micrometer and nanometer sizes. The kinetics of the photopolymerization and degree of conversion were studied by real time FTIR (RT-FTIR) and photo differential scanning calorimetry (photoDSC) experiments. Increasing silver particle concentration reduced the conversion of double bonds. Formulations containing silver nanoparticles had lower conversion than those with silver flakes. At higher filler loading, it was necessary to employ dual curing technique (UV followed by thermal) to get optimum conversion.

Introduction

The benefits and advantages of UV-curing technologies are very well known and have been frequently mentioned since the early development of industrial applications. These are rapid cure, nonpolluting and solvent-free system compared to thermal drying, enhanced product durability, low energy requirements, low temperature operation, and small space requirements.[1]

Screen printing ink is one of the important application fields of radiation curing technology. Important application areas of these types of inks are radio frequency identification (RFID) antennas, printed-circuit boards, smart card components, smart labels and printed electronics.[2] Conductive inks are typically formulated with a polymer binder system, solvent, and contain micro-sized conductive metal particles, such as silver or copper, to provide conductivity. However, most of the commercial UV-curing ink formulations are highly crosslinked systems, which cannot flow by the application of heat and pressure after UV-curing. In many applications screen-printed conductive inks may also be used as a substrate for attachment to another conductive device. For example, a "bond pad" can be printed using the conductive ink and then using heat and pressure this bond pad can be attached to another similar bond pad or metallic conductor. In order for good electrical contact to be formed during this bonding process, the polymer binder system must be able to flow under the influence of heat and pressure.[3]

A novel screen printable, radiation "curable" ink formulation has been developed where the binder system consists of a low volatility monofunctional liquid acrylate monomer, dissolved acrylate/ methacrylate polymer, and a photoinitiator. Different types of silver particles are dispersed in the binder system to achieve required conductivity. The advantage of this system is that it remains thermoplastic even after UV "curing" and can be softened at a later stage upon application of heat and pressure.

The objective of the present work was to obtain an insight of the UV-curing behavior of these novel ink formulations through real time FTIR (RTIR) and photoDSC experiments.

Experimental

Materials

The monomer tetrahydrofurfuryl acrylate (THFA) was obtained from Sartomer and was used as received. The photoinitiator (PI) Irgacure 369 was obtained from Ciba and the thermal initiator benzoyl peroxide (BPO) was obtained from Aldrich and both were used as received. Solid poly(methyl methacrylate) (PMMA) resin having average molecular weight of 120,000 was purchased from Aldrich. Silver flakes (Agfl) having dimensions less than 10 micron were purchased from Aldrich. Silver nano-powder (AgNP) having average diameter 150 nm was obtained from Inframat Advanced Materials.

Formulations

Each formulation contained 4% of PI based on the weight of the monomer. Formulations which can be cured by dual curing method contained 2% of benzoyl peroxide (BPO) as thermal initiator in addition to the PI. Formulations containing different concentrations of PMMA were prepared by the addition of PMMA resin to the liquid monomer followed by stirring under slightly heated condition. All the formulations containing silver particles were prepared with a mixture of 1 wt.% PMMA in THFA. Each formulation was prepared by sonicating the silver particles in the PMMA-monomer mixture. The sonication time was varied between 1 and 4 hours until a homogeneous suspension was obtained. This was then followed by the addition of the required amount of initiators and further sonication for approximately 5 minutes of the whole mixture.

Characterization

Real-time Fourier transform infrared (RTIR) experiments were performed using a Nicolet Magna-IR 850 spectrometer Series II with detector type DTGS KBr, with a UV optic fiber mounted in a sample chamber. The light source was a 100-Watt compact arc DC mercury vapor lamp. The UV light intensity at the sample position was measured using a UV Power Puck II from EIT Inc. and the result is shown in Table1. This setup monitors the reaction of the functional groups *in situ* as the photopolymerization proceeds. Liquid solution/ suspension sample was coated on KBr window in thin films. The coating was then exposed to UV radiation in the FTIR beam for 15 sec. at 6 scans per second and all the experiments were performed in air. The percent conversion of acrylate double bond is calculated by equation 1 as follows:

$$\text{Degree of conversion} = \{((A_{810})_0 - (A_{810})_t)/(A_{810})_0\}*100 \quad \ldots\ldots\ldots\ldots(1)$$

Table1. RTIR UV-lamp intensity

UV radiation type	mW/cm^2
UVA	57.44
UVB	44.994
UVC	0.00
UVV	25.21

PhotoDSC experiments were performed utilizing a Q1000 DSC (TA Instruments) modified with the photocalorimeter accessory (PCA); the light intensity was approximately 40mW/cm^2. All the photoDSC experiments were done in a nitrogen atmosphere. Sample sizes ranged between 4.00 and 6.00 mg. The samples were irradiated by UV light for specific period of time at 25°C. For samples where dual curing mechanisms were present, after the UV irradiation period, the temperature was raised to 120°C by a temperature ramp of 50°C/min. and then allowed to stand isothermally for 5 min. to obtain the residual heat of reaction. For acrylate double bond conversion, the heat of polymerization reaction was taken as 86.1 KJ/mol.[4] The theoretical heat of reaction can be calculated by the following equation (2):

$$\Delta H_{theoretical} = (B*C*D)/MW \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(2)$$

where, A = J/g of formulation
B = number of sites /molecule of monomer
C = fraction of monomer in the formulation
D = J/mole of reactive site
MW = g/ mole for monomer

The monomer conversion during photoDSC experiments is given by equation 3 as follows: [1]

$$\% \text{ Conversion} = (\Delta H_{exp.}/ \Delta H_{theoretical})*100 \dots\dots\dots\dots(3)$$

Results and Discussion

Formulation

The binder system consists of a monofunctional, low volatility, liquid acrylate monomer (tetrahydrofurfuryl acrylate), dissolved PMMA resin and a photoinitiator (Irgacure 369). The structure of the monomer is shown in Figure1. The photoinitiator Irgacure 369 is a combination of alpha-amino ketones. The dissolved PMMA increases the viscosity of the liquid binder system before curing and this helps to stabilize the dispersion of silver particles against sedimentation.
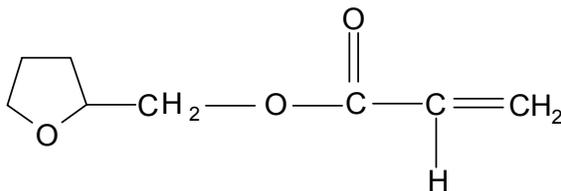
Figure 1. Structure of THFA monomer.

RTIR experiment

In the RTIR experiments, the =C-H out of plane band at 810 cm^{-1} was monitored for
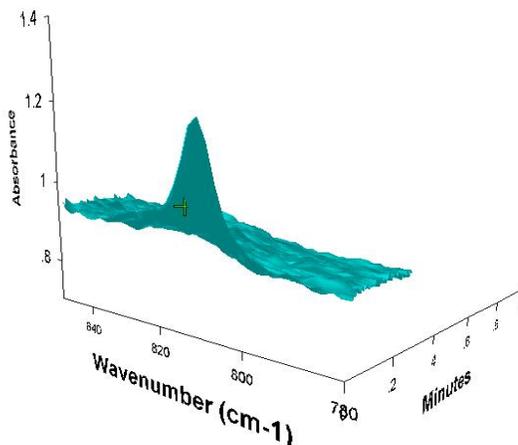
Figure 2. RTIR experiment: Disappearance of the IR peak as a function of time.

studying the acrylate conversion.[5] Figure 2 shows the decrease in absorbance of the acrylate double bond peak at 810 cm^{-1} with time as a result of photopolymerization as recorded in a typical RTIR experiment.

Solid PMMA resin was dissolved in THFA monomer to get sufficient viscosity in the system to prevent the sedimentation of the silver particles. However, it was necessary to see the effect of PMMA resin on the curing of THFA. Figure 3 shows the percent conversion vs. time curves for different THFA-PMMA combinations. It can be observed from Figure 3 that the formulation containing no PMMA resin has slightly slower rate of conversion compared to those containing different amounts of PMMA resin in the formulations. Additionally, it can be seen that conversion vs. time curves of all the formulations containing PMMA resin overlap with each other indicating that the amount of PMMA does not have much influence on the curing behavior of this system. Figure 4 shows the final conversion of the different formulations after 5 sec. of UV radiation. It can be seen that for all the formulations more than 90%
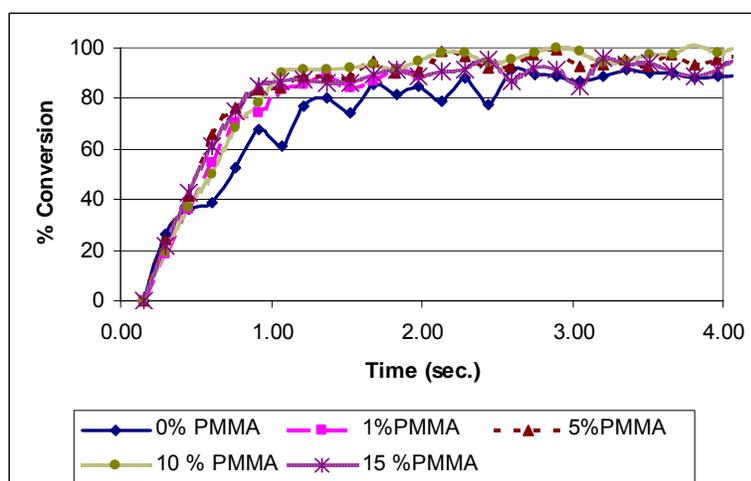
Figure 3. Effect of PMMA on the photopolymerization behavior of THFA as obtained by RTIR experiment.
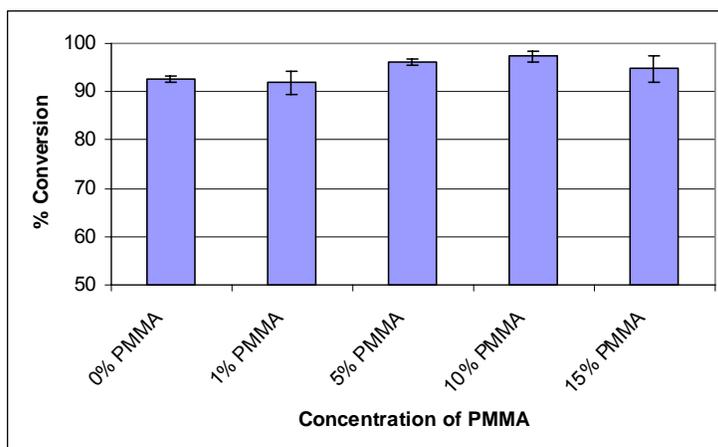
Figure 4. Final conversion of THFA containing different concentrations of PMMA as obtained by RTIR.

conversion was reached. THFA is one of the fastest curing commercially available monofunctional acrylate monomers and the photoinitiator selected in these formulations also has fast curing characteristics.[3] Thus the combination of THFA with this PI gives fast curing and high conversion which are very desirable since by the addition of silver particles in the formulation it is expected that both the rate of reaction and final conversion would diminish.

PhotoDSC experiment

In the photoDSC experiments, final conversion was determined from the total heat flow by integrating the area under the curve and the relative maximum rate of polymerization was measured from exotherm peak maxima.[1, 6] Figures 5 and 6 show the photoDSC traces of the
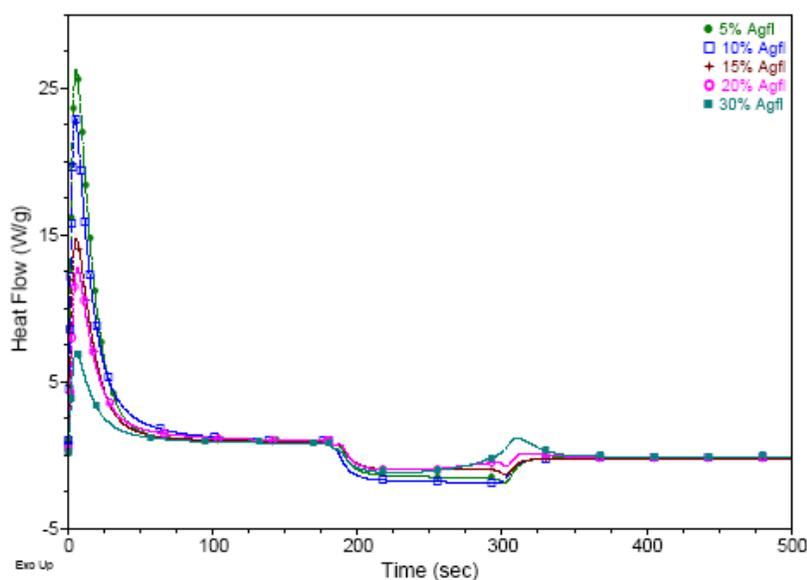
Figure 5. Effect of silver flakes on the photopolymerization behavior of THFA as determined by photoDSC.

formulations containing different concentrations of silver flakes and silver nanopowder respectively. The initial exotherm in the graph indicates the polymerization reaction by UV radiation and the exotherm(s) indicate the residual polymerization through thermal initiation. Also, it is evident from the graphs that with increasing concentration of silver particles, the exotherm for UV-curing decreases and this effect is more pronounced in the formulations containing silver nanopowders. This can be explained from the fact that silver particles strongly absorb the incident radiation and thereby reduce the UV light intensity for the photoinitiator molecules. Also it has been reported that the shape of the conductive particles determines the final degree of polymerization in radiation curing.[7]

Figures 7 and 8 show the individual photoDSC traces for 20 wt.% silver nanopowders and flakes, respectively. The temperature profile during the experiment is also shown as a function of time. It can be seen that in both the cases the temperature increases slightly during the photopolymerization step and slightly higher temperature was obtained with the formulation containing silver flakes, which is possibly due to higher rate of polymerization reaction and/ or
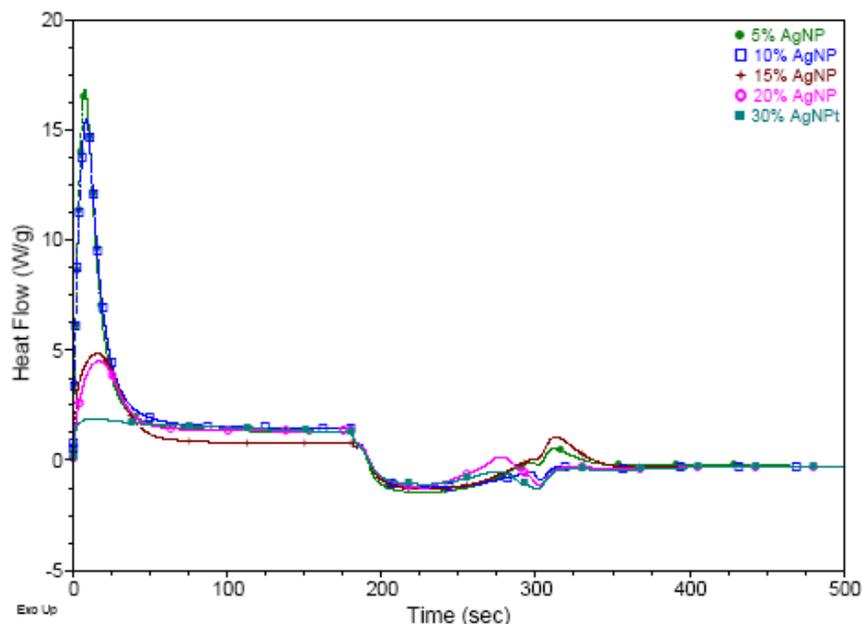
Figure 6. Effect of silver nanopowders on the photopolymerization behavior of THFA as determined by photoDSC

higher conversion by UV curing. Additionally, it is evident from the temperature profile of both the graphs that the temperature rise in the UV curing step was not sufficient to trigger the thermal polymerization by BPO initiator. Hence the initial exotherm of photoDSC trace is solely due to photopolymerization. For the heat curing step, the formulation containing silver nanopowder showed two distinct and larger exotherm peaks, whereas the formulation containing silver flakes exhibited a single and relatively small exotherm peak indicating a lower degree of thermal curing.
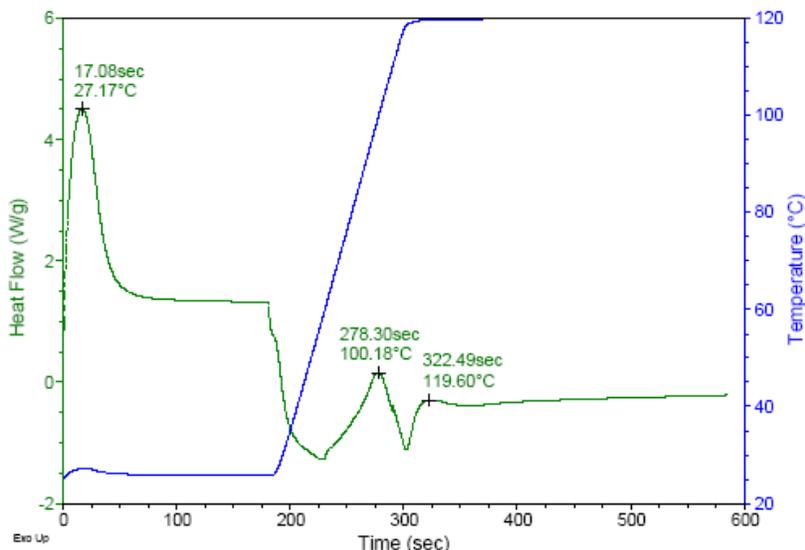
Figure 7. PhotoDSC trace of the sample containing 20 wt.% of silver nanopowder
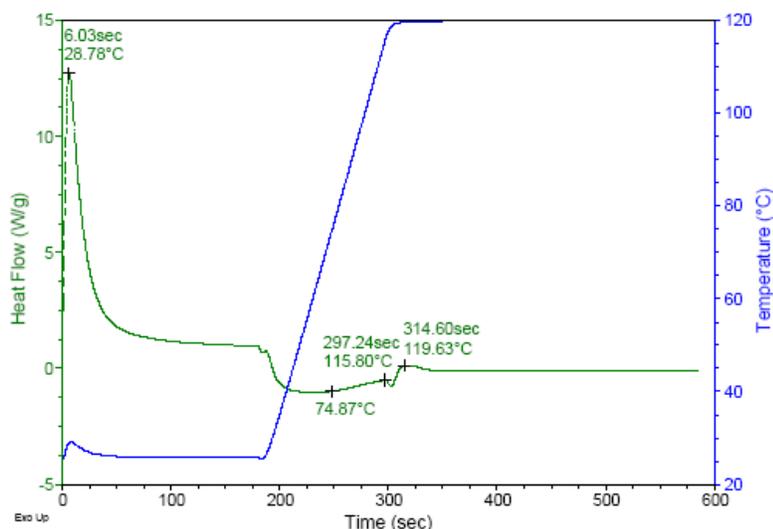
Figure 8. PhotoDSC trace of the sample containing 20 wt.% of silver flakes.

Table 2. Conversion data for different formulations obtained from photoDSC traces.

Formulation	% Conversion by UV curing	% Conversion by heat curing	Total conversion
0% silver particles	91.55	2.14	93.69
5% AgNP	55.63	3.71	59.34
5% Agfl	89.83	1.81	91.64
10% AgNP	58.83	3.56	62.39
10% Agfl	88.94	4.48	93.42
15% AgNP	35.81	15.39	51.20
15% Agfl	63.19	1.70	64.89
20% AgNP	33.57	13.96	47.53
20% Agfl	59.27	6.02	65.29
30% AgNP	21.01	10.88	31.89
30% Agfl	43.36	16.16	59.52

Table 2 shows the conversion data for different formulations and Figure 9 shows the percent conversion data of different formulations by the initial UV curing step and by heat curing step. All of the formulations exhibited the expected trend of decreasing conversion with increasing silver particle content in the formulation. It can be seen from the table that for the formulations containing silver flakes, the total conversion remained unaffected up to 15% of silver flakes loading. The percent conversion by UV curing remained relatively unchanged up to 10% of silver flakes loading after which it started decreasing with increasing amount of silver flakes in the recipe. Additionally, it can be observed that the contribution of heat curing towards the total conversion remained negligible up to formulations containing 15% silver flakes after which it started increasing with decreasing amount of UV curing. As already mentioned, the decrease the in the UV curing with increasing amount of silver particle in the recipe is much more pronounced with silver nanopowder compared to silver flakes. The amount of photopolymerization was drastically reduced upon addition of even 5% of silver nanopowder

and this could not be compensated by heat curing. Thus the overall conversion steadily decreased with increasing concentration of silver nanopowder.
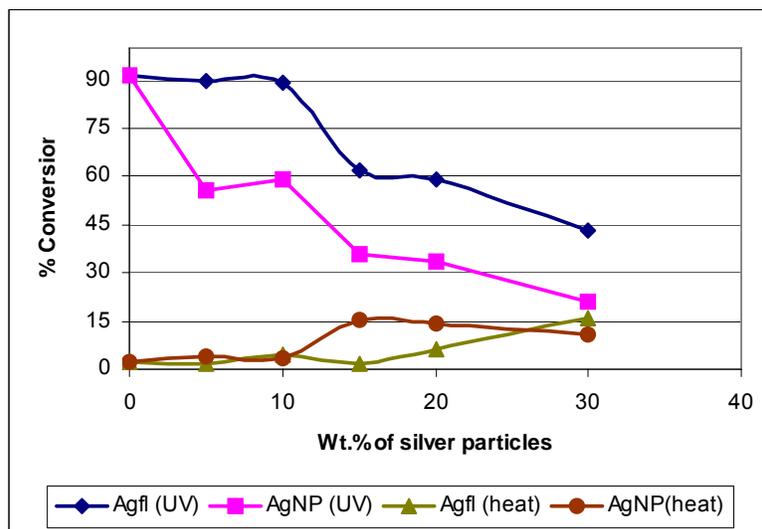
Figure 9. Conversion by UV-curing and heat curing as determined by photoDSC.
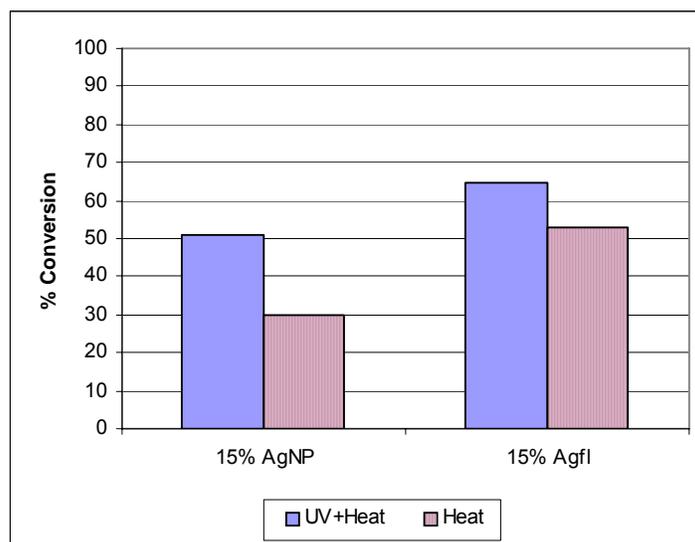
Figure 10. Comparison of dual curing method and heat curing only method.

In another photoDSC experiment, only the thermal polymerization step was allowed occur without the initial photopolymerization step for the two formulations containing 15 wt% of silver flakes and nanopowder. The percent conversion values obtained from this experiment were compared with those obtained from the combination of photopolymerization and thermal polymerization values. The results are shown in Figure 10. It can be seen that in both the cases, there was significantly higher degree of conversion when dual curing mechanism was employed compared to the thermal curing only method.

Figure 11 shows the H_{max} values of different formulations as a function of the amount of silver particles in the recipe. As already mentioned, the H_{max} value indicates the maximum rate of photopolymerization of a particular recipe.[2, 5] From the graph, it can be readily observed that the rates of photopolymerization decrease steadily with increasing concentration of silver particle for both flakes and nanopowder.
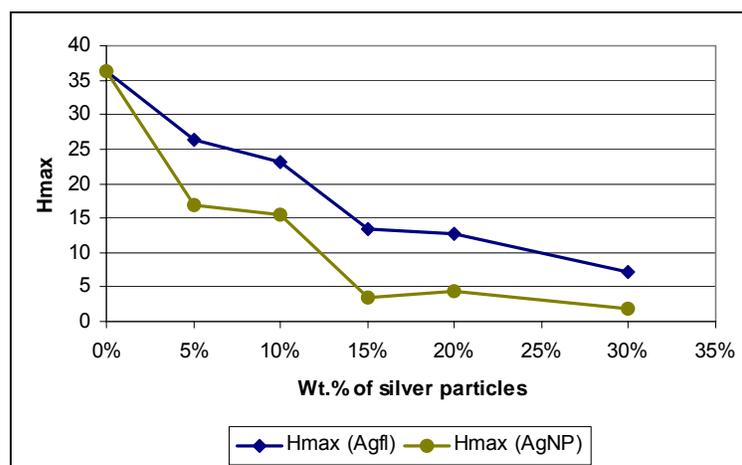
Figure 11. Comparison of the initial rate of photopolymerization of different formulations by H_{max} values.

Conclusions

Radiation curable conductive ink formulations were made by combining monofunctional liquid acrylate monomer dissolved methacrylate polymer and silver particles. It was observed from RTIR experiments that the combination of THFA monomer and the photoinitiator Irgacure 369 gave fast curing characteristics and high conversion. Dissolved PMMA resin slightly increased the rate of conversion compared to the formulation containing no PMMA. However, the rate of conversion remained unaffected by concentration of PMMA in the formulation. All the formulations without any silver particles showed a high degree of conversion.

In photoDSC experiment the UV curing step was followed by a thermal curing step at 120°C to get the residual polymerization in the later stage. It was observed that both the rate of UV-polymerization and final conversion was decreased by the addition of silver particles and this effect is more pronounced with silver nanopowder compared to silver flakes. To check the performance of dual curing compared to single heat curing step, two samples were examined by allowing the heat curing only without prior photocuring. It was observed that for both cases higher conversions were achieved in the dual curing method.

Acknowledgement

and should not be interpreted as necessarily representing the official policies or endorsements, either expressed or implied of the Defense Microelectronics Activity(DMEA).

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